



Short Note

1,3-Bis(2,6-diisopropylphenyl)-2-trichloromethylimidazolidine

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Abstract: A new chloroform adduct of the *N*-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr) has been prepared via C–H bond activation of the chloroform at the carbene carbon. This redox product was crystallized and was characterized by ^1H and ^{13}C -NMR spectroscopy, elemental analysis (EA), and single-crystal X-ray diffraction. The ^1H and ^{13}C -NMR spectroscopic data are in agreement with the crystal structure. Density functional theory (DFT) calculations were performed as a means for comparison to experimental data and the computational results are in agreement with those obtained experimentally.

Keywords: *N*-heterocyclic carbene; NHC; chloroform; carbon-halogen compound; single-crystal X-ray diffraction; crystal structure

1. Introduction

A carbene is a type of chemical species that comprises a neutral carbon atom which is bonded to any two (2) 'R' groups, while simultaneously bearing a pair of non-bonded valence electrons (Figure 1).

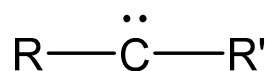


Figure 1. General structural formula representative of a carbene.

Carbenes can exist in either a singlet or a triplet state. A singlet carbene is one that is said to be spin-paired, where the lone pair of electrons on the carbon atom reside in the same orbital, leaving an extra empty orbital on the carbon center, whereas a triplet carbene has electrons of the same spin residing in two valence orbitals and is generally referred to as a diradical (Figure 2).

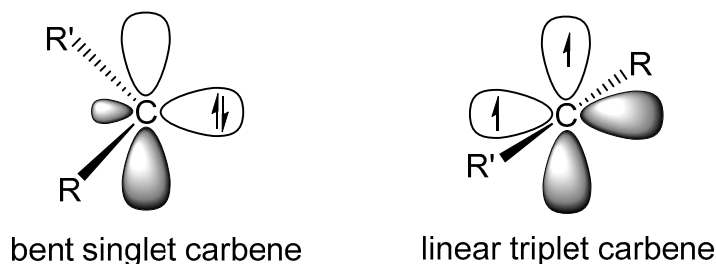


Figure 2. General structural representation of a singlet carbene and a triplet carbene.

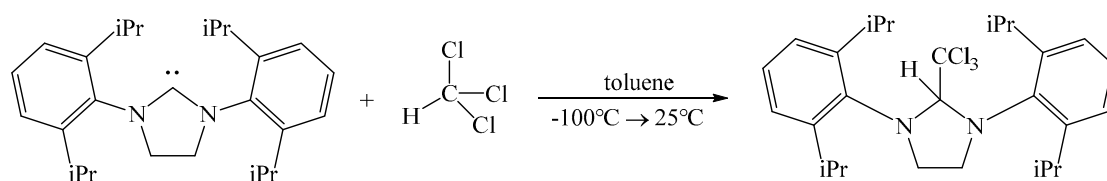
Bertrand and Reed [1] stabilized singlet carbenes through the use of main group elements, which led to the discovery of the first phosphino silyl carbenes [2], followed by other novel singlet carbenes [3–5]. However, it was report of the first ‘bottleable’ crystalline *N*-heterocyclic carbene (NHC) [6] that initiated a new paradigm in synthetic chemistry [7]. NHCs are often preferred over other types of carbenes due to their stability and ease of synthesis. In particular, these stable carbenes are able to activate small molecules, and help stabilize highly reactive intermediates [8].

The molecule presented here comes from the reaction of a well-known carbene (SIPr carbene) with chloroform to form SIPr(H)CCl₃, and while there are examples of similar compounds in the literature such as 1,3-bis(2,4,6-trimethylphenyl)-2-(trichloromethyl)imidazolidine [9], and 1,3-diphenyl-2-(trichloromethyl)imidazolidine [10], this particular derivative has yet to be reported outside of the patent literature, and to the best of our knowledge, this is the first reported single crystal structure of a chloroform-bound carbene. Although carbenes are typically used as ligands for transition metals [11–15], or as nucleophilic organic catalysts [16–25], these carbene derivatives that contain an (H)CCl₃ bound at the carbene C2 position have been found through reductive thermolysis, to give free carbene for reaction with metals [26].

2. Results and Discussion

2.1. Synthetic Discussion

SIPr carbene was reacted with chloroform under cold (−100 °C) conditions to produce SIPr(H)CCl₃ in 26% isolated yield (Scheme 1).



Scheme 1. Reaction scheme for the synthesis of SIPr(H)CCl₃.

The addition of chloroform to SIPr carbene was initially attempted at room temperature; however, the crude material product was much less pure (by ¹H-NMR spectroscopic analysis). Once the reaction was attempted at low temperature, the purity of the crude product increased significantly. This material was highly soluble in all solvents tried (Et₂O, THF, toluene, pentane). Purification by cooling (−35 °C) a saturated room temperature pentane solution gave the title compound in low isolated yield due to its high solubility. Elemental analysis of the purified compound gave adequate results (<0.4% difference between calculated and measured values). When analysis by high resolution ESI mass spectrometry was performed, the parent ion was not observed, however what was observed was the stable imidazolidinium cation, formed by the loss of [CCl₃][−] from the title compound (Figure S3).

2.2. X-ray Crystallography

The molecule crystallizes as colorless, rectangular-shaped crystals in the space group *P*2₁/*c* and contains one molecule in its asymmetric unit (Figure 3). The crystal structure has C1–Cl1, C1–Cl2, and C1–Cl3 bond lengths of 1.770(2), 1.7800(19), and 1.780(2) Å respectively, which are in line with the average C_{sp}³–Cl bond length of 1.768(22) Å for interactions of similar nature (mean bond length of 1300 structures found in CSD Release 5.387, May 2017) [27]. In addition, the structure has C1–C2, C2–N1, and C2–N2 bond lengths of 1.576(3), 1.442(2), and 1.450(3) Å, respectively. The C1–C2 length is similar to other 1,1'-diamino substituted 2,2',2''-trichloroethane fragments (1.548(12) Å) whereas the C2–N1 and C2–N2 lengths are statistically indistinguishable from the literature value of 1.469(14) Å for a C_{sp}³–N_{sp}³ bond length [28]. It is also apparent that the NHC backbone has a slight twist occurring to

account for the steric bulk introduced by the presence of the 2,6-diisopropylphenyl substituents and the CCl_3 group attached to C2. These bulky groups also have an impact on the position of H2 relative to the isopropyl methine hydrogen atoms (H23 and H11) that H2 faces; the $\text{H} \cdots \text{H}$ distances are ca. 1.92 and 1.99 Å. These short distances can be attributed to the steric pressure of the CCl_3 group pulling on the C2 atom as well as the CCl_3 group pushing the adjacent isopropyl groups away, thus causing the isopropyl groups on the opposite side of the heterocycle to be pushed in towards H2.

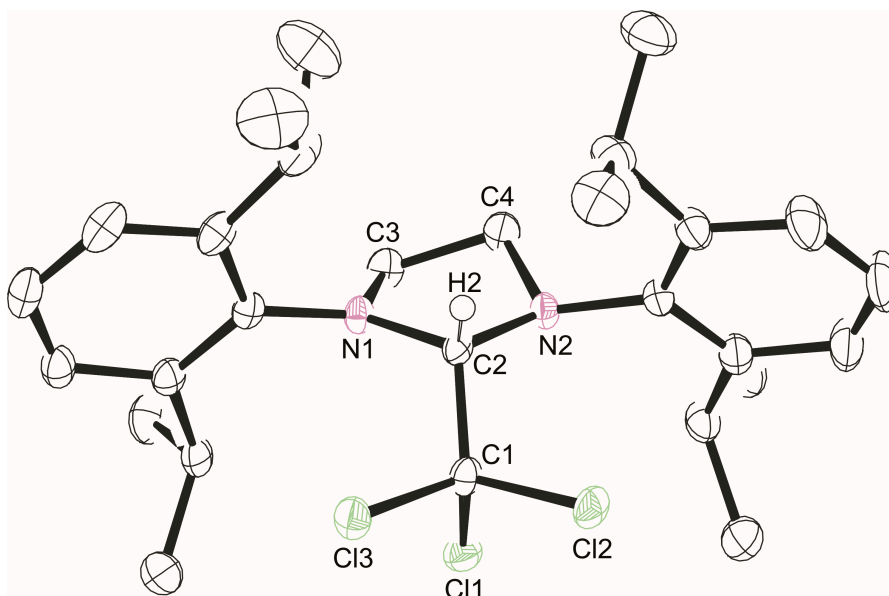


Figure 3. Crystal structure of SIPr(H)CCl_3 . Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity, with the exception of the proton at the C2 position.

Comparing the crystal structure of the presented adduct to that of the free SIPr carbene [29], the C2–N1 and C2–N2 bond lengths are longer in the SIPr(H)CCl_3 molecule than those of the carbene (1.442(2) and 1.450(3) Å for SIPrHCCl_3 vs. 1.3458(16) and 1.3474(16) Å for the free carbene). This difference in bond length can be attributed to the three electronegative chlorine atoms. Given their electronegativity, these atoms are inductively electron-withdrawing, and will draw electron density out of the NHC ring, thus resulting in elongated C–N bonds within the ring.

Additionally, the SIPr(H)CCl_3 adduct has N1–C3 and N2–C4 bond lengths of 1.464(2) and 1.462(3) Å, whereas the free carbene has N1–C3 and N2–C4 lengths of 1.4793(17) and 1.4790(17) Å. In this case, the carbene has slightly longer bond lengths than those of the SIPr(H)CCl_3 adduct. Again, this can be reasoned out by understanding that the aforementioned inductive effects from the chlorine atoms will have a more significant effect on the C–N bonds that are nearest to the carbene center (C2 position). While some of the density in the NHC ring is being drawn toward the chlorine atoms and elongating the C2–N1 and C2–N2 bonds, the N1–C3 and N2–C4 bond lengths will shorten by a small amount, thus resulting in shorter bond lengths.

Density functional theory (DFT) calculations were performed on the presented molecule and the results are summarized below in Table 1. Not that the calculated bond lengths are not significantly different than those found in the crystal structure.

Table 1. Selected bond lengths (Å) and angles (°) for the SiPr(H)CCl₃ adduct as obtained experimentally from the crystal structure, as well as the calculated values from a DFT calculation.

Bond or Angle Type	Crystal Structure		DFT (B3LYP/6-311G(2d,p))	
	Exp. Bond Length (Å) or Angle (°)	Avg. Bond Length (Å) or Angle (°)	Calc. Bond Length (Å) or Angle (°)	Difference (%)
C–Cl	1.770(2)	1.777(3)	1.8049	1.5
	1.7800(19)			
	1.780(2)			
C _{carbene} –N	1.442(2)	1.447(4)	1.4549	0.5
	1.450(3)			
C _{backbone} –N	1.464(2)	1.463(4)	1.4647	0.1
	1.462(3)			
C _{carbene} –C	1.576(3)	–	1.5978	1.4
N–C–N	103.23(15)	–	103.73	0.5
C–N–C	110.26(15)	110.81(2)	110.45	0.3
	111.36(15)			
N–C _{carbene} –C	111.22(15)	112.61(2)	112.81	0.2
	113.99(16)			

3. Materials and Methods

3.1. General Methods, X-ray Crystallography Sample Collection, and Computational Details

All manipulations were carried out under an inert atmosphere of dry nitrogen or argon gas using either standard Schlenk techniques or in an mBraun inert atmosphere glovebox unless otherwise stated. NMR spectra were recorded at 298 K on a 300 MHz spectrometer (Bruker, Milton, ON, Canada) and are reported in ppm. The ¹H-NMR spectrum was collected in a deuterated solvent and referenced [30] internally to a residual protio (¹H) solvent relative to tetramethylsilane, TMS (δ = 0 ppm). The ¹³C-NMR spectrum was referenced [30] internally to the respective deuterated solvent in which it was collected relative to TMS (δ = 0 ppm). All reagents were purchased from Sigma-Aldrich (Oakville, ON, Canada) and used as received, unless otherwise stated. Chloroform (anhydrous grade, Sigma-Aldrich) was further dried over molecular sieves. Pentane (Caledon Laboratory Chemicals, Halton Hills, ON, Canada) and tetrahydrofuran (anhydrous and inhibitor free, Caledon Laboratory Chemicals, Halton Hills, ON, Canada) were dried by passing the solvent through alumina columns, further dried over KH overnight, and was then passed through another plug of alumina to yield clean, dry solvent. Elemental analysis was performed by the Centre for Environmental Analysis and Remediation (CEAR) facility at Saint Mary's University using a Perkin Elmer 2400 II series Elemental Analyzer.

Under inert conditions, crystals were prepared by suspending them in paratone-N oil on a microscope slide. A single crystal was attached to the tip of a MiTeGen loop with paratone-N oil and cooled to 125 K. Measurements were made on a Bruker APEX2 CCD equipped diffractometer (30 mA, 50 mV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K. The initial orientation and unit cell were indexed [31] using a least-squares analysis of a random set of reflections collected from three series of 0.5° wide scans, 10 s per frame and 12 frames per series that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 5 s frames and 416 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT software [32], which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarization effects. Data processing and a multi-scan absorption correction was applied using APEX3 software package [31]. Structures were solved using direct methods [31] and all non-hydrogen atoms were refined anisotropically using the ShelXLE [33] graphical user interface and SHELXL [34]. Hydrogen atoms were included at geometrically idealized positions and were fixed

(Ar-H, C-H, CH₂) or in the case of methyl groups, the dihedral angle of the idealized tetrahedral CH₃ fragment was allowed to refine, and coupled with isotropic temperature factors. In the case of the methine hydrogen atoms that were directed at one another (H2, H11, and H23) of the C(H)CCl₃ and isopropyl groups, these were placed in geometrically fixed positions, while letting the C-H distances refine. This reduced the intramolecular distances between these hydrogen atoms, giving a better model overall. Figures were made using ORTEP-3 for Windows [35]. Additional crystallographic information has been provided in Tables S1–S5.

Calculations were performed using Gaussian09W [36]. The molecule was optimized at the B3LYP/6-311G(2d,p) level of theory and a frequency calculation verified the structure was a stationary point.

3.2. Synthesis of SIPr(H)CCl₃

In a glovebox, in a 250 mL round-bottomed Schlenk flask equipped with a magnetic stirring bar, was placed chloroform (10 mL, anhydrous grade, Sigma-Aldrich) and THF (50 mL). In a 50 mL dropping funnel equipped with a Teflon stopcock and a 10 mL round-bottomed flask attached to the base of the funnel, was placed SIPr carbene (0.9963 g, 2.538 mmol) which was pre-dissolved in THF (45 mL). Both pieces of glassware were sealed with septa and taken out of the glovebox and into a fume hood. At this time, a cold bath comprised of ethanol and liquid nitrogen was prepared until it reached a temperature of −100 °C. The round-bottomed flask containing the chloroform/THF solution was evacuated and refilled three times with argon before being lowered into the cold bath. Under the flow of argon, the septum was replaced by the dropping funnel and the carbene/THF solution was added dropwise to the flask containing the chloroform solution (~30 min). The solution turned a faint yellow color upon addition of the carbene solution. Following the complete dropwise addition of the carbene solution, the dropping funnel was replaced by the original septum and the flask was removed from the cold bath and allowed to warm to room temperature with the continuous stirring of the solution (~1 h). The flask was then returned to the glovebox and left to stir overnight (18 h) during which time the solution went from a faint yellow color to a light green color. The following morning, volatiles were removed *in vacuo*, resulting in orange-red colored solids. ¹H-NMR spectroscopy confirmed the formation of the desired product. The remaining solids were dissolved in pentane (10 mL) and filtered into a 20 mL scintillation vial using a glass pipette containing a layer of diatomaceous earth for recrystallization. The vial was placed in a freezer for 72 h during which time the formation of large, orange-brown colored crystals occurred. The pentane was decanted from the crystals into a clean 20 mL glass vial and they were washed with small amounts of cold pentane (2 × 2 mL). A ¹H-NMR spectrum was obtained on the crystals and the spectrum indicated that the crystals were not the desired product. A crystal was submitted for single X-ray diffraction analysis to determine its composition and the structure was found to be *N*-(2,6-diisopropylphenyl)-*N*-[2-(2,6-diisopropylphenylamino)ethyl]formamide (ring opened SIPr formed as a result of hydrolysis with water). At this point, the decanted pentane was concentrated to half of the original volume (5 mL) and placed back in the freezer for 48 h which resulted in the formation of small, colorless, rectangular shaped crystals. Again, the pentane was decanted into a clean 20 mL glass vial and the crystals were washed with small amounts of cold pentane (2 × 2 mL). A ¹H-NMR sample was run on the crystals and the spectrum confirmed the formation of the SIPr(H)CCl₃ product. At this time, a crystal suitable for X-ray diffraction analysis was submitted. Yield: 0.3316 g, 0.6052 mmol, 26%.

SIPr(H)CCl₃. ¹H-NMR (300 MHz, 298 K, C₆D₆, Figure S1) δ: 7.22–7.08 ppm (m, Ar-H, 6H), 5.75 (s, CHCCl₃, 1H), 4.13 (sept., CH(CH₃)₂, 2H), 3.76 (sext., NHC-CH₂, 2H), 3.57 (sept., CH(CH₃)₂, 2H), 3.25 (sext., NHC-CH₂, 2H), 1.42 (d, CH(CH₃)₂, 12H), 1.28 (d, CH(CH₃)₂, 6H), 1.25 (d, CH(CH₃)₂, 6H). ¹³C-NMR (300 MHz, 298 K, C₆D₆, Figure S2) δ: 150.2 ppm (s, *o*-C), 146.0 (s, *o*-C), 141.4 (s, *ipso*-C), 127.5 (s, *p*-C), 125.3 (s, *m*-C), 124.6 (s, *m*-C), 107.5 (s, CCl₃), 91.2 (s, CHCCl₃), 54.2 (s, NHC-CH₂), 28.9 (s, CH(CH₃)₂), 28.1 (s, CH(CH₃)₂), 26.0 (s, CH(CH₃)₂), 25.8 (s, CH(CH₃)₂), 24.5 (s, CH(CH₃)₂), 23.9 (s, CH(CH₃)₂). Elem. Anal. Calcd for C₂₈H₃₉N₂Cl₃: C 65.94, H 7.71, N 5.49 %; Found: C 66.31, H

7.68, N 5.68 %. HRMS (ESI TOF): $[M - CCl_3, C_{27}H_{39}N_2]^+$ found 391.312337. $[C_{27}H_{39}N_2]^+$ requires 391.310776. Single-crystal X-ray diffraction for $C_{28}H_{39}N_2Cl_3$ ($M = 509.96$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 8.2621(6)$ Å, $b = 18.7132(14)$ Å, $c = 17.9937(14)$ Å, $\alpha = 90^\circ$, $\beta = 93.3260(10)^\circ$, $\gamma = 90^\circ$, $V = 2777.3(4)$ Å³, $Z = 4$, $T = 125(2)$ K, $\mu(MoK\alpha) = 0.348$ mm⁻¹, $D_{calc} = 1.220$ g/cm³, 19144 reflections measured ($1.571^\circ \leq \theta \leq 26.000^\circ$), 5405 unique reflections ($R_{int} = 0.0661$, $R_{sigma} = 0.0605$) which were used in all calculations. The final R_1 was 0.0466 ($I > 2\sigma(I)$) and wR_2 was 0.1202 (all data). CCDC 1574779 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

4. Conclusions

A new chloroform adduct of the saturated NHC SIPr has been prepared where the H–C bond of the chloroform has added at the carbene center via an oxidative addition reaction. The compound was crystallized and characterized by ¹H and ¹³C-NMR spectroscopy, EA, and single-crystal X-ray diffraction. DFT calculations were performed on the title molecule and the calculated bond lengths and angles were compared to the experimental values and are in good agreement with one another.

Supplementary Materials: The following are available online <http://www.mdpi.com/1422-8599/2017/4/M962>, Figure S1: ¹H-NMR spectrum of SIPr(H)CCl₃, Figure S2: ¹³C{¹H} NMR spectrum of SIPr(H)CCl₃, Figure S3: High resolution ESI mass spectrum of SIPr(H)CCl₃, Table S1: Atomic coordinates and equivalent isotropic displacement parameters of SIPr(H)CCl₃, Table S2: Bond lengths and angles for SIPr(H)CCl₃, Table S3: Anisotropic displacement parameters for SIPr(H)CCl₃, Table S4: Hydrogen coordinates and isotropic displacement parameters for SIPr(H)CCl₃. Table S5. XYZ atomic coordinates for SIPr(H)CCl₃ optimized at the B3LYP/6-311G(2d,p) level of theory.

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Author Contributions: D.L.S. and J.D.M. designed the experiment. D.L.S. did the synthetic work, performed measurements, and prepared and analyzed the crystal sample and data. D.L.S. and J.D.M. wrote the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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